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HIROFUJI SATOSHI**(54) FILM, MULTILAYER FILM, PACKAGING MATERIAL AND PACKAGED MATERIAL**

(57)Abstract:

**PURPOSE:** To provide the subject product composed of a resin composition containing an ethylene-vinyl alcohol copolymer and an inorganic filler, having a specific property and enabling the boiling sterilization without causing the deterioration of the appearance and the gas-barrierness of the packaging material.

**CONSTITUTION:** The objective film is composed of a layer of a composition containing (A) 50-95wt.% of an ethylene-vinyl alcohol copolymer and (B) 50-5wt.% of an inorganic filler. The component A in the layer contains a number of regions containing two-dimensional thin layers of the component B laminated parallel to the plane of the composition layer. The flake diameter of the component B in the region is  $\leq 30\mu\text{m}$  and the weight-average aspect ratio is  $\geq 3$ . The moisture-permeability of the composition layer satisfies the formula  $[W \text{ is moisture permeability (g.} 30\mu\text{m}^2\text{.day) at } 40^\circ\text{C and relative humidity difference of 90\%; E is ethylene content (mol\%) of the component A; } A0=1.105\times 10^3; A1=-8.15\times 10; A2=2.42; A3=-3.535\times 10^{-2}; A4=2.53\times 10^{-4}; A5=-7.091\times 10^{-7}]$  and the dimensional change of the layer is -2.5 to +2.5% (after treatment in air at  $T_m -40^\circ\text{C}$  for 60min).

**\* NOTICES \***

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Industrial Application]The film of the resin composition in which this invention consists of an ethylene-vinyl alcohol system copolymer (it is described as the following EVOH), and an inorganic filler, And the multilayer film which makes said constituent layer an interlayer and has a layer of damp-proof thermoplastics in this interlayer's inside-and-outside layer, And the voile sterilization which consists of said film or a multilayer film or the packing material for retort sterilization, and this packing material are filled up with contents, and it is considered as a sealed package object, and this is continuously related with the packed body by which voile sterilization or the preservability which carried out retort sterilization, heat contraction nature, and appearance were improved.

[0002]

[Description of the Prior Art]Conventionally, in the food packaging body, although a metal can, a glass bottle, various plastic containers, etc. are used as the container, the plastic container is used as various kinds of containers for food packing from the field of the flexibility of lightweight nature and a gestalt, shock resistance, or cost in recent years.

[0003]However, the oxygen transmission quantity as a material a metal can and a glass bottle to being zero a plastic container, In packaging forms, such as a pouch of especially the for the object for voile sterilization, and for retort sterilization, and lid material, In under the conditions on which heat and moisture act simultaneously, the gas barrier property, since oxygen gas barrier property is especially insufficient, [ as / in the hot water germicidal treatment or the steam sterilizing process which are in the limelight as a food distribution gestalt especially in recent years ] The actual condition is the above permissible oxygen's advancing into a container, and degradation by oxygen of contents foodstuffs taking place, becoming a problem in respect of preservability, such as flavor of foodstuffs, and freshness, and used only for the limited use.

[0004]Namely, although there are polyvinylidene chloride system polymers as a representative of the gas-barrier-property resin used as a pouch or lid material till the present, it does not necessarily have sufficient oxygen gas barrier property, From viewpoints (quality of a decomposition product by improper [ recycle employment ] and incineration is made into the cause of acid rain) of the latest global environment problems, it is not desirable.

[0005]In order that EVOH which is the representation of other gas-barrier-property resin may also prevent

the above-mentioned point, the plastic container which consists of multilayer structure which laminated EVOH by the thermoplastic resin layer and the adhesive resin layer is taken out to the commercial scene, but. The actual condition was that there is a problem which is described below and the performance as a container for food packing which should be satisfied is not obtained.

[0006]Namely, in such a multilayer-structure object, although EVOH shows good gas barrier property under low humidity, Heat and moisture act simultaneously, that is, when using it under an elevated temperature and high humidity, moisture infiltrates into an EVOH layer through an outer layer, and the fault that the gas barrier property of an EVOH layer falls rapidly for this reason is pointed out. [ as / in especially voile sterilization or retort sterilization ] In the gestalt of the multilayer film especially represented by a pouch, lid material, etc., the appearance change by heat shrinking was also a big problem.

[0007]Influence of the moisture in such voile sterilization or retort sterilization is made small, and in order to improve the fault that gas barrier property falls, the multilayer layered product which provided the protective layer which blended the drier is indicated to JP,57-170748,A, JP,62-6508,B, etc. However, since the moisture which infiltrated into this protective layer by this processing touched a gas barrier layer, the moisture to which it stuck once shifted to the gas barrier layer, and there was anxiety to which the function of a gas barrier layer falls.

[0008]The constituent which becomes JP,1-253442,A from EVOH and polyamide system resin is made into an interlayer, An outer layer has the statement of the multilayer packed body which makes a inner layer low moisture-permeable resin (for example, polypropylene) in high-moisture-permeability resin (for example, polyamide), although the use of the above-mentioned germicidal treatment has a fixed effect, gas barrier property is now -- there is a problem of it not being enough, and the film which consists of a constituent which consists of EVOH and polyamide system resin having a large dimensional change at the time of heating, and worsening appearance change of a multilayer packed body.

[0009]Although the multilayered container which provided the thermoplastic resin layer at least in one side of the EVOH layer which blended inorganic substances, such as talc, is indicated to JP,61-242841,A, It is not necessarily easy to obtain the packed body which was excellent in the preservability after voile sterilization or retort sterilization depending on a method which is indicated here.

[0010]By the way, although EVOH containing talc is indicated as a constituent which blended talc with EVOH and is publicly known at JP,51-21822,B or JP,62-143980,A, for example, The hermetic container for food packing is obtained from the multilayer layered product which makes this constituent one layer as shown in this invention, and the technical idea of the food packaging body produced by processing this under heat and the conditions on which moisture acts simultaneously is not indicated continuously.

[0011]

[Problem(s) to be Solved by the Invention]This invention prevents aggravation of the appearance of the packed body after voile sterilization or retort sterilization among the problems of said conventional technology, and controls degradation of gas barrier property further to the minimum. Carry out a deer and the purpose of this invention fills up with contents the packing material which consists of an EVOH film especially a multilayer film which uses damp-proof thermoplastics as an inside-and-outside layer, and makes an EVOH layer an interlayer, and this film, It is in providing the packed body by which it was considered as the sealed package object and voile sterilization or the preservability which carried out retort sterilization, heat contraction nature, and appearance were continuously improved in this, especially a food

packaging body.

[0012]

[Means for Solving the Problem] This invention persons consist of EVOH and an inorganic filler, as a result of repeating research wholeheartedly, And a resin composition which specified a dispersion state of an inorganic filler and with which it is moreover satisfied of the following (I) is made into an interlayer, It is considered as a hermetic container using a multilayer packed body which has an inside-and-outside layer of damp-proof thermoplastics, and a food packaging body produced by carrying out germicidal treatment of this under heat and conditions on which moisture acts simultaneously does not have deterioration of contents continuously, and appearance of a multilayer packed body after germicidal treatment was improved, and it found out that it was the outstanding food packaging body.

[0013] Namely, this invention consists of a layer of a resin composition which consists of 50 to 95 % of the weight of ethylene-vinyl alcohol system copolymers, and 50 to 5 % of the weight of inorganic fillers, Many fields where a two-dimensional film has laminated an inorganic filler in parallel with the direction of a stratification plane of said layer substantially are included in said copolymer in said layer, And a diameter of a weighted mean flake of an inorganic filler in this field is 30micro or less, a weighted mean aspect ratio is three or more, moisture vapor transmission of said layer satisfies a following (I) type further, and it is a rate of a dimensional change (in the air) further. Melting point-40 \*\*, a film whose value measured after 60-minute processing is -2.5%~+2.5%, And it is the packed body which filled up with contents a container which consists of a multilayer film which makes a layer of said resin composition an interlayer and has damp-proof thermoplastics in this interlayer's inside-and-outside layer and this film, or a multilayer film, and this container.

$$W \leq \sum_{i=0}^5 (A_i \cdot E^i) \quad (I)$$

Here, content (mol %) of moisture vapor transmission [ in / in W / temperature of 40 \*\* and 90% of a relative humidity difference ] (g.30 micro/m<sup>2</sup> and day) and an ethylene ingredient of said copolymer [ in / in E / said film or intermediate layer resin ] and A<sub>i</sub> (i= 0-5) are constants given below. It is shown that E<sup>i</sup> is the i-th power of E.

A<sub>0</sub> = 1.105x10<sup>-3</sup> A<sub>1</sub> = -8.150x10 A<sub>2</sub> = 2.420 A<sub>3</sub> = -3.535x10<sup>-2</sup> A<sub>4</sub> = 2.530x10<sup>-4</sup> A<sub>5</sub> = -7.091x10<sup>-7</sup> [0014] Hereafter,

this invention is explained concretely. EVOH which is one of the ingredients which form a film or an interlayer used for this invention is an ethylene-vinyl ester system copolymer saponification thing, it is preferred for an ethylene content that it is [ 20-60 mol % ], and it is 25-55-mol % preferably. If an ethylene content is smaller than 20-mol %, while a water resisting property and moisture resistance will fall, gas barrier property under high humidity is spoiled, and stress-cracking-proof nature falls, and maintenance of a good melting working characteristic also becomes difficult. On the other hand, if larger than 60-mol %, although a water resisting property and moisture resistance will improve, original outstanding gas barrier property worsens. Anyway, as materials for a package etc., it becomes unsuitable. A saponification degree of a vinyl ester ingredient needs to be more than 95 mol %, and is 98-mol % preferably. Less than [ 95 mol % ], thermal stability worsens, and a fault which gel tends to generate at the time of melting processing

arises, and gas barrier property and oil resistance also fall, and it becomes impossible for a saponification degree to hold the original characteristic of EVOH, and it becomes difficult to enjoy an effect of this invention. Although vinyl acetate is raised here as a typical thing as vinyl ester, other vinyl ester, for example, low-grade or higher-fatty-acid vinyl ester, (vinyl propionate, vinyl pivalate, etc.) can be used. One or more sorts of said vinyl ester may be used, and it can also use two or more sorts.

[0015]In this invention, as EVOH, 20-60 mol of ethylene content%, it is more than saponification degree 95 mol %, and vinylsilane content% of 0.0001-0.5 mol of silicon content EVOH can use it for satisfaction more to the purpose of this invention. As an olefin nature unsaturated monomer containing silicon, a conventionally publicly known monomer which is indicated by JP,61-290046,A etc. can be used. For example, vinyltrimetoxysilane, vinyltriethoxysilane, vinylmethyldimethoxysilane, vinyltriacetoxysilane, a vinyl tripropionyloxy silane, etc. are mentioned. Although this silicon content is selected according to each purpose, 0.0001-0.5-mol %, especially 0.001-0.1-mol% of the range is preferred.

[0016]Melt indices (a measured value which was measured on conditions of temperature of 190 °C and 2160 g of load according to ASTM D1238 65T; it is described as MI below) of EVOH are 0.1-50g/10 minutes, although there is no restriction in particular. Unless the purpose of this invention is checked, by a little copolymerization monomers, EVOH said to this invention may denaturalize and as a monomer for denaturation, Propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, Acrylic ester, methacrylic acid ester, maleic acid, phthalic acid, Itaconic acid, higher-fatty-acid vinyl ester, alkyl vinyl ether, N-vinyl pyrrolidone, N-normal butoxy methacrylamide, N-(2-dimethylaminoethyl) methacrylamide or the 4th class ghost of those, N-vinylimidazole, or the 4th class ghost of its can be illustrated.

[0017]Next, an inorganic filler which is another [ which forms a film or an interlayer used by this invention ] ingredient is explained. As an inorganic filler, a diameter of a weighted mean flake is 30micro or less in particle diameter, and it is important to have three or more weighted mean aspect ratios. A modification effect becomes less enough when blend nature with EVOH and membrane formation nature after a blend will worsen if a diameter of a weighted mean flake becomes larger than 30 micro, and an aspect ratio is smaller than three. It is checked by a scanning electron microscope that a value of a raw material inorganic filler before mixing an above-mentioned diameter of a weighted mean flake and an aspect ratio of an inorganic filler to EVOH, and a value of an inorganic filler which exists in a multilayer packed body do not almost have a difference.

[0018]Therefore, in this invention, a diameter of a weighted mean flake of an inorganic filler and a weighted mean aspect ratio mean a value of an inorganic filler which is a value of an inorganic filler before kneading to EVOH, or exists in a multilayer packed body. 15micro or less of diameters of a weighted mean flake of an inorganic filler are 5micro or less still more suitably suitably. Although not limited in particular for a lower limit, 0.5 micro is 1micro still more suitably suitably. About a weighted mean aspect ratio, it is ten or more still more suitably five or more suitably. It is not limited in particular for upper limit.

[0019]With a diameter of a weighted mean flake in this invention, a granular material (here thing of an inorganic filler) is classified by various kinds of Micro sieves or sieves of an opening. It is a value equivalent to opening  $L_{50}$  of a Micro sieve or a sieve which 50% of the weight of full weight of a granular material which plotted the result in a Rosin-Rammler diagram, and with which measurement was presented passes. That is, it is defined as the diameter L of a weighted mean flake of a granular material by (II) or a (III)

formula.

$L=L_{50}$  (in the case of a Micro sieve) (II)

$L=2^{1/2} \cdot L_{50}$  (in case of sieve) (III)

Here, among granular materials, it is a sieve, is classified about a portion with a large particle size, and is classified by Micro sieve about a portion with a fine particle size.

[0020] On the other hand, weighted mean aspect ratio  $\alpha$  of a granular material in this invention is the diameter  $L$  of a weighted mean flake, and a value computed using a (IV) type from weighted mean flake thickness  $d$  of a granular material measured by the following methods.

$\alpha=L/d$  (IV)

[0021] (IV) Weighted mean flake thickness  $d$  of a granular material in a formula, C.E. Water surface simple grain child film method {C. by Capes's and others report by E. Capes and R.C. Coleman. Ind. Eng. Chem. Fundam., Vol. 12, No. 1, and p. 124-126 (1973)}. It is a value computed from a (V) type using the occupation area  $S$  in the water surface of a flake measured.

$d=W/(\rho \cdot (1-\epsilon) \cdot S)$  (V)

[0022] It is the share when weight of a granular material with which  $W$  presented measurement here, and  $\rho$  take specific gravity of a granular material and, as for  $(1-\epsilon)$ , a granular material takes a closest packing state on the water surface, and, generally 0.9 was used when calculating about a granular material.

[0023] Although talc, clay, a sericite, a glass flake, mica, etc. are raised as an inorganic filler in this invention, talc and clay are preferred in respect of shock resistance and thermoforming nature.

[0024] As a blending ratio in this resin composition that forms a film or an interlayer, it is especially chosen as the range of these 50 to 5 % of the weight of inorganic fillers, and profit out of 40 to 20% of the weight of a range 50 to 15% of the weight to these 50 to 95 % of the weight of EVOH(s). If an addition of this inorganic filler exceeds 50 % of the weight, mobility at the time of melting, the moldability of mixed material, and intensity will fall, An effect over appearance maintenance of a multilayer packed body which makes an interlayer this constituent after germicidal treatment under conditions on which film production nature also falls to and a modification effect, i.e., preservability, heat, and moisture of contents, acts simultaneously at less than 5 % of the weight becomes less enough.

[0025] Although this constituent that consists of these 50 to 95 % of the weight of EVOH(s) and these 50 to 5 % of the weight of inorganic fillers of this invention is used as a film or an interlayer, this packed body -- mostly, over the whole region, in EVOH, an inorganic filler does not condense and, It is one of the important requirements especially for this invention to have the decentralized structure that many fields which a two-dimensional film has laminated in parallel with an interlayer's direction of a stratification plane substantially are included, and this feature may be judged from observation by a scanning electron microscope. That these a majority of fields are included means that this field exists to a stratification plane or a thickness direction in a film or an interlayer not only over one place but over at least two or more places.

[0026] Next, how to obtain this resin composition that forms a film or an interlayer is described. In order to distribute uniformly, and to become a two-dimensional film substantially, to laminate in parallel with an interlayer's direction of a stratification plane and to make it exist, without an inorganic filler condensing in

EVOH, kneading operation of this resin composition is very important. A method (melt kneading method) of carrying out melt kneading of EVOH and the inorganic filler (especially talc) above the melting point of EVOH is raised first. As this method, a powdered thing and pellet type thing and an inorganic filler of EVOH The usual mixer, For example, mix in a Henschel mixer and a super mixer, or mix an inorganic filler to EVOH melt, and master pellets are built, This is mixed to a powdered thing of EVOH, a pellet type thing, and melt, and then a method of kneading this mixture above the melting point of EVOH is raised. Without mixing EVOH and an inorganic filler beforehand as mentioned above, EVOH and an inorganic filler can be directly introduced into a kneading machine, and can also be kneaded. Although continued type kneading machines, such as a continuous system intensive mixer and a kneading type twin-shaft extruder (the direction or a different direction), are the optimal as a kneading machine for obtaining a constituent which has advanced distribution without floc of an inorganic filler, Batch type kneading machines, such as a Banbury mixer, an intensive mixer, and a pressurized kneader, can also be used.

[0027]In this, a continuous system intensive mixer can be raised to the purpose of this invention as most desirable thing. As a model marketed, there is CIM by the product FCM Japan Steel Works made by Farrell or Kobe Steel KCM, Ltd., NCM, LCM, or ACM. A device which has a 1 axis extrusion machine under these kneading machines actually, and carries out extrusion pelletizing simultaneously is desirable. A 2 axis extruding kneading machine which has a kneading disk or a rotor for kneading, for example, TEX of the Japan Steel Works, Ltd., ZSK of Werner & Pfleiderer, TEM of Toshiba Machine Co., Ltd., and PCM of IKEGAI Steel are also used for the purpose of kneading of this invention.

[0028]In using these continued type kneading machines, a rotor and a role with important shape of a disk are played. Especially a gap (clearance) with a mixing chamber, a rotor chip, or a disk chip is important, and its 1-5 mm is the optimal as tip clearance. In order to obtain a constituent which has the good dispersibility of this invention, it became clear that it was required as specific energy of a kneading machine to knead desirably 0.1-0.8 kWh/kg 0.05 kWh /or more kg.

[0029]Specific energy \*\* energy (amount of used electricity; KW) used for kneading by a kneading throughput per hour, it asks, and the unit is kWh/kg. In order it is required in order for kneading with a value in which specific energy is higher than a value adopted by the usual kneading to obtain a constituent of this invention, and to consider it as specific energy of 0.05 kWh/kg or more, It is insufficient just to raise number of rotations of a kneading machine, and it is preferred to cool a constituent under kneading with a jacket etc., to lower temperature, and to raise viscosity. kneading temperature -- discharge resin temperature of an exit of a kneading part -- the range of the melting point of EVOH - the melting point of +80 \*\* -- it is the range of the melting point - the melting point of +60 \*\* more suitably. 50-1200 rpm of number of rotations of a rotor of a kneading machine is 100-1200 rpm preferably. As for a kneading-machine chamber inside diameter, a not less than 30-mm thing is mentioned preferably not less than 20 mm. Also when blending inorganic fillers (talc etc.) with resin which forms an inside-and-outside layer, this melt kneading method can be enforced.

[0030]Another method of obtaining this resin composition that forms a film or an interlayer is the method (solvent method) of blending an inorganic filler with EVOH using a solvent of EVOH(s), such as methyl alcohol/water, n-propyl alcohol / drainage system. Which method of a method of adding an inorganic filler in a solution which EVOH dissolved as turn of combination, a method of adding and dissolving EVOH at the solvent which an inorganic filler distributed conversely, or a method of adding simultaneously may be

used. After combination is deposited in strand shape indicated by Japanese JP,725,520,B, and a method of separating EVOH which contains an inorganic filler is used suitably. If needed, by a publicly known method, after deposit isolation processes rinsing, acid treatment, etc., and, subsequently dries. Although it applies to a solvent method correspondingly, inorganic fillers (talc etc.) may be added by a process step of saponification before obtaining EVOH.

[0031]When obtaining this resin composition that forms a film or an interlayer, it does not interfere, even if it adds other polymer, such as a plasticizer, an unguent, an antioxidant, colorant, and an ultraviolet ray absorbent, in the range by which a operation effect of this invention is not spoiled.

[0032]next, being important in this invention -- a film of this invention, or an interlayer's moisture vapor transmission -- said (I) type -- it is the following (I') formula and satisfying the following (I'') formula still more suitably suitably. Although a multilayer packed body obtained using as an interlayer this EVOH constituent obtained with a described method has a desired improvement effect, it may not necessarily be enough. Then, a film or an interlayer whose moisture vapor transmission consists of this resin composition small in this way as EVOH as a result of this invention persons' inquiring wholeheartedly, A useful thing was found out, especially when it was used an elevated temperature like voile sterilization and retort sterilization processing, and under highly humid and the gas barrier property of EVOH fell.

$$\begin{matrix} 5 \\ W \leq \sum (B_i \cdot E^i) \\ i=0 \end{matrix} \quad (I')$$

$$\begin{matrix} 5 \\ W \leq \sum (C_i \cdot E^i) \\ i=0 \end{matrix} \quad (I'')$$

Moisture vapor transmission [ in / here / in W / temperature of 40 \*\*, and 90% of a relative humidity difference ] (g.30 micro/m<sup>2</sup> and day), Content (mol %), B<sub>i</sub> (i= 0-5), and C<sub>i</sub> (i= 0-5) of an ethylene ingredient of an ethylene-vinyl alcohol system copolymer [ in / in E / a film or intermediate layer resin ] are a constant given below. Moisture vapor transmission was measured according to JIS Z 0208. It is shown that E<sup>i</sup> is the i-th power of E.

B<sub>0</sub>= .9.100x10<sup>-2</sup>B<sub>1</sub>=-6.712x10B<sub>2</sub>= 1.993B<sub>3</sub>=-2.911x10<sup>-2</sup>B<sub>4</sub>= 2.083x10<sup>-4</sup>B<sub>5</sub>=-5.840x10<sup>-7</sup>C<sub>0</sub>= .6.000x10<sup>-2</sup>C<sub>1</sub>=-4.193x10C<sub>2</sub>= 1.188C<sub>3</sub>=-1.667x10<sup>-2</sup>C<sub>4</sub>= 1.156x10<sup>-4</sup>C<sub>5</sub>=-3.163x10<sup>-7</sup>[0033]Methods of giving such moisture vapor transmission in this invention involve a method of existing [ 5-500 ppm ] a phosphoric acid root (PO<sub>4</sub><sup>-3</sup>), for example in EVOH. As a compound which has a phosphoric acid root here, phosphoric acid, phosphoric acid soda, phosphoric acid 2 hydrogen sodium, phosphoric acid 1 hydrogen disodium, etc. are raised. As abundance of a phosphoric acid root, not less than 5 ppm is preferred, and 500 ppm or less are preferred.

[0034]Both important things in this invention are that a rate of a dimensional change (value measured under melting point-40 \*\* and 60 minutes in the air) is -2.5% - +2.5% of within the limits at the time of heating of both a lengthwise direction of a film or an interlayer, and a transverse direction. Even if a rate of



a dimensional change is larger than these values at the time of heating and it is small, EVOH transforms an obtained multilayer packed body in the case of use under an elevated temperature like voile sterilization and retort sterilization processing (wrinkles, sag, torsion, etc.), and appearance of a multilayer packed body gets worse. When this invention persons are not clear enough about a mechanism as a result of inquiring wholeheartedly, but a rate of a dimensional change becomes in a mentioned range at the time of heating of an interlayer who consists of this resin composition, A very useful thing was found out to prevention from aggravation of appearance of a multilayer packed body used at an elevated temperature like voile sterilization and retort sterilization processing. A rate of a dimensional change at the time of heating is a value computed by following (VI) type from length change by heat-treatment for 60 minutes at melting point-40 \*\* in [ of a lengthwise direction of a center of a film of a 10 cm angle, and a transverse direction ] the air. A lengthwise direction and a transverse direction are directions (often expressed as TD) respectively right-angled in the film production direction (often expressed as MD) and the film production direction of a film here.

$J = (M - N) / N$  and 100 (VI)

[0035] A rate of a dimensional change when J is heat-treated in the air and heat-treated under 60 minutes at melting point-40 \*\* here (%), M is the length (cm) of a lengthwise direction of a center of a film after heating, or a transverse direction, N is the length (cm) of a lengthwise direction of a center of a film before heating, or a transverse direction, and in calculation of a (VI) type, when M is the length of a lengthwise direction, N also makes N lateral length, when the length of a lengthwise direction and M are lateral length. The melting point is the fusion endothermic peak temperature (\*\*) of EVOH of an EVOH constituent in DSC measurement (a part for heating-rate/of 10 \*\*).

[0036] Manufacturing methods of a film which gives such a rate of a dimensional change involve the following methods. From an extruding press machine which uses a screw or a plunger, melting extrusion of the resin composition pellet is carried out by T die or a ring die, and the resin composition used for this invention can fabricate it. In this case, this resin composition has high hygroscopicity, if it carries out extrusion molding as it is when moisture regain is 0.5% or more, it will foam to it, and it cannot obtain a good film. In order to obtain a good film on which it does not foam, it is desirable for moisture regain to dry to 0.25% or less preferably, for the purpose, it dries a resin composition pellet at 90-120 \*\*, and supplies extrusion from a hopper which carried out the nitrogen purge of the dried pellet continuously. It is necessary to decide as an extrusion-molding temperature according to the melting point of EVOH of this resin composition. although it depends for the melting point of EVOH on the ethylene content and saponification degree greatly, and the melting point of EVOH becomes high so that a saponification degree is so high that an ethylene content is small -- temperature setting of a 20 - 120 \*\* elevated temperature [ melting point ] as molding temperature -- it is 30-70 \*\* preferably. If molding temperature is too low, load which melting of this resin composition becomes uneven, and a BUTSU-like thing generates, and melt viscosity goes up, and is applied to a screw increases, and it is not desirable. On the other hand, if molding temperature is too high, the thermal stability of EVOH of this resin composition will fall, and a fall of extrusion operation time by generating of a scorch of gelling by heat deterioration and a screw portion will be caused, and it is not desirable. a melted object of this resin composition -- said T die carried out or a ring die -- melt extruding -- it cools with a roll for cooling, or a cooling ring continuously, and a film of this invention is obtained. As a temperature in the case of cooling, 40-100 \*\* is 50-95 \*\* preferably. A film after

cooling may heat-treat.

[0037] It is free to blend other thermoplastics, a bulking agent, a plasticizer, an unguent, a drier, an antioxidant, a thermostabilizer, an ultraviolet ray absorbent, colorant, etc. with a resin composition used for this invention in a range from which the purpose of this invention is not prevented. Especially a thing for which a kind of a metal salt [ of higher fatty acid, such as a hydrotalcite system compound and calcium stearate, ], magnesium acetate, hinder phenol system, and hinder amine system thermostabilizer or two sorts are added as a measure against gelling occurrence prevention is preferred. It may be preferred to blend a drier and here as a drier, Salts of hydrate formation nature, i.e., salts which absorb moisture as crystal water, division phosphoric acid 1 sodium, Phosphates, such as phosphoric acid disodium, trisodium monophosphate, phosphoric acid 3 lithium, and sodium pyrophosphate, Salts (for example, salts, such as sodium borate and sodium sulfate, an anhydride of those) of the anhydride and other hydrate formation nature, other hygroscopic compounds (for example, sodium chloride, sodium nitrate, sugar, silica gel), a water-absorbing resin, etc. are raised.

[0038] In this invention, although said film can also be used by a monolayer, it is more effective as wrapping for voile sterilization or retort sterilization to use as a multilayer film which makes this layer an interlayer, among these has damp-proof thermoplastics in an outer layer. This multilayer film is described below.

[0039] As resin which forms an inside-and-outside layer which consists of damp-proof thermoplastics, hydrophobic resin, especially polyolefin system resin are raised as a typical thing. As polyolefin system resin, polyethylene of high density, semi-gross density, or low density, Polypropylene of high density, semi-gross density, or low density, vinyl acetate, acrylic ester, Or polyethylene which carried out copolymerization of the alpha olefins, such as a butene, a hexene, and 4-methyl-1-pentene, Ionomer resin, polypropylene which carried out the graft copolymerization of the ethylene, Or polypropylene which carried out copolymerization of the alpha olefins, such as ethylene, a hexene, and 4-methyl-1-pentene, poly-1-butene, poly-4-methyl-1-pentene, or denaturation polyolefine that made a maleic anhydride etc. act on above-mentioned polyolefine is included. In this, polypropylene (PP) fits the purpose of this invention most.

[0040] As resin which furthermore forms an inside-and-outside layer, poly (ethylene terephthalate), Poly (ethylene naphthalate), poly (butylene terephthalate), Polystyrene system resin or polycarbonate system resin represented by poly (ethylene terephthalate/isophthalate) etc., such as polyester system resin, polystyrene, a styrene butadiene copolymer, and a styrene isoprene copolymer, is raised. Even if resin which forms the above-mentioned inside-and-outside layer may be the same as that also of an inside-and-outside layer and differs, it is not cared about. This talc mentioned above in the range by which a moldability is not spoiled may be blended with resin which forms these layers.

[0041] A multilayer film of this invention can be conventionally manufactured with various kinds of laminating methods, such as the publicly known co-extruding method, the dry laminate method, the sand laminating method, and extrusion laminating method. When creating some layers of a multilayer packed body of this invention by the co-extruding method, a usual method of laminating an interlayer and an inside-and-outside layer on both sides of a layer of adhesive resin is adopted. As adhesive resin, what is necessary is just what does not cause delamination in a practical use stage, although limitation in particular is not carried out -- unsaturated carboxylic acid or its anhydride -- an olefin system polymer (for example, polyethylene.) A denaturation olefin system polymer containing a carboxyl group produced by combining

with a copolymer which makes polyolefines, such as polypropylene and polybutene, and an olefin a subject chemically (for example, an addition reaction, a grafting reaction) is mentioned. Specifically Maleic anhydride graft modified polyethylene, maleic anhydride graft denaturation polypropylene, One sort or two sorts of mixtures chosen from a maleic anhydride graft denaturation ethylene-ethyl acrylate copolymer and a maleic anhydride graft denaturation ethylene-vinylacetate copolymer are mentioned as a suitable thing. It is also possible to mix EVOH to these adhesive resin in the range by which an effect of this invention is not spoiled. A scrap by which it is generated when manufacturing a multilayered container of this invention can also be used for an inside-and-outside layer which consists of that of damp-proof thermoplastics in the co-extruding method as a raw material. A scrap can also be used as an independent layer with an inside-and-outside layer. It will not be limited, especially if a method of pasting together a film beyond three sorts or it of an outer layer, an interlayer, and an inner layer is common and layer indirect arrival power is enough as adhesives for dry laminates, when adopting the dry laminate method.

[0042]When it is used as a film of this invention, a multilayer film, a packing material, and a packing material especially for voile sterilization or retort sterilization, the feature is demonstrated most. As a use of film packaging material, lid material, pouches, a vacuum package, skin packaging, a deep-drawing package, a rocket package, etc. are raised. A method of carrying out seal seal with a heat seal method is suitable for lid material in a container which made a gas barrier material a subject. it is said that a dimensional change is small at the time of heating, contraction stress becomes small, and it does not have modification of a container in the case of voile sterilization or retort sterilization processing while lid material of this invention has advanced possession nature -- very -- good -- better -- it has the strong point for \*\*. Pouches are used with a gestalt of a three-way-type seal, a four-quarters seal, a pillow, a gazette, a standing pouch, etc. It can also be used in a form of a bag in box.

[0043]8micro-60micro are preferred for a film of this invention, or an interlayer's thickness, and it is 10micro-40micro still more suitably. 10micro-250micro are preferred for thickness of a layer of damp-proof thermoplastics of an inside-and-outside layer respectively, and it is 20micro-100micro still more suitably. 30micro-600micro are preferred for total thickness of a multilayer film respectively, and it is 50micro-250micro still more suitably.

[0044]a container which uses a packing material of this invention in a form of lid material and pouches -- voile sterilization -- although retort sterilization processing is carried out, a hot water heat-treatment method and conditions publicly known as these disposal methods are employable. As for retorting, various methods, such as a recovery type, a substitution type, a shower type, and a spray type, are adopted.

[0045]An inside is made into a degassing state by a publicly known means if needed after filling up with contents, especially foodstuffs a packing material of this invention mentioned above, Or after inactive gas, such as nitrogen gas and carbon dioxide, replaces an inside, it seals by heat seal or other means, Then, germicidal treatment is carried out with hot water or a steam (especially an elevated temperature, autoclave sterilization) like retorting especially carried out at 105-135 \*\* under temperature conditions, for example over what is called boiling treatment 100 \*\* or less or 100 \*\*, and a packed body can be obtained.

[0046]As contents with which it fills up, foodstuffs are mainly raised. Foodstuffs of precooked or half-cooking which are eaten as it is or are warmed in advance of eating as foodstuffs here are suitable. Next, an example of sterilization foodstuffs is shown. Precooked curry, precooked HAYASHI, beef stew, borsch, meat sauce, It boils by sweet-and-sour pork, sukiyaki, Chinese bean jam, chop suey, potatoes stewed with

pork, Japanese pot-au-feu, and asparagus \*\*, Various soup, such as a sweet corn, a mushroom, tuna cream \*\*, consomme, and potage, miso soup, miso soup with pork and vegetables, Kenchin-style tofu, pork, and vegetable soup, rice, rice with vegetables and meat, fried rice, pilaf, rice porridge, spaghetti, a side, Foodstuffs for addition, such as Japanese noodles, ramen noodles, a noodle, base of rice with vegetables and meat, and base of Chinese noodles. Boil and An azuki bean, sweet red-bean soup with rice cakes, boiled peas with honey and bean jam, a meatball, a hamburger, a beefsteak, Roast pork, pork saute, corned beef, a ham, a sausage, roast fish, roast meat, grilled chicken, roast chicken, pork catsup, fish meat smoked fish, bacon, boiled fish paste, a pudding, jelly, sweet bean paste, and various pet food are raised. Although an example explains this invention still more concretely below, this invention does not receive limitation at all by this. A part means a weight section.

[0047]

[Example]

In the degree of saponification of 31 mol of example 1 ethylene-content % and a vinyl acetate component, 99.5-mol MI% 1.6g/80 copies of granular materials of EVOH for 10 minutes, 20 copies of talc granular materials of 15 were carried out after preliminary mixing, 3 micro and a weighted mean aspect ratio carried out high-speed mixing within the Henschel mixer, and the diameter of a weighted mean flake obtained the mixture. Kneading extrusion pelletizing was carried out using the two-step biaxial-anisotropic continuous extrusion machine which has two steps of mixing rotors and has a deaeration mechanism between two rotors by a mixing chamber 30 mm in inside diameter succeedingly, and the 1 axis extrusion machine made to connect with this, and the pellet of the constituent was obtained. The tip clearance with a mixing chamber of the mixing rotor adopted at this time is 3 mm, kneading temperature (outlet temperature) was carried out in the 205-230 \*\* range, and rotor number of rotations was carried out in 300-450 rpm and the range of 0.1-0.3 kWh/kg of specific energy.

[0048]About the above-mentioned constituent, it changed into the anhydrous state substantially and the melting point  $T_m$  was measured using Mettler DSC30 (a part for heating-rate/of 10 \*\*). A result is shown in Table 1. Subsequently, after drying this blend pellet at 105 \*\* (moisture regain was 0.2%), The film was produced using the extrusion machine and the casting roll (cooling roller) with a skin temperature of 90 \*\* which have a coat hanger die (temperature of 230 \*\*) of a full flighted screw with a diameter of 40 mm and 500-mm width, and the non-oriented film (f) of the 30-micro-thick constituent was obtained. The film piece of the 10-cm angle which uses the film production direction (lengthwise direction) and a direction (transverse direction) right-angled to it as the neighborhood from this film was cut down, and it heat-treated at melting point-40 \*\* for 60 minutes, and asked for the dimensional change at the time of heating from length change of the lengthwise direction and the transverse direction before and behind processing. A result is shown in Table 1. About this film (f), moisture vapor transmission was measured on condition of 40 \*\* and 90%RH according to JIS Z 0208. Under \*\* which writes this EVOH layer in the nitric acid solution of a decinormal, it heated for 3 hours and 95 \*\* of phosphoric acid roots in the filtrate were measured with ion chromatography. These results are combined with Table 1 and shown.

[0049]Next, this film (f) was used for the interlayer, the polypropylene film (100micro in thickness) was used for the inside-and-outside layer, dry laminate was carried out, and the multilayer film of three layers was obtained. As adhesives for dry laminates, the bamboo rack A-385 (made by Takeda Chemical Industries, Ltd.) was used, and Takenate A-10 (made by Takeda Chemical Industries, Ltd.) was used for base resin

as a hardening agent. The coverage of adhesives was  $4.0 \text{ g/m}^2$ . Care of health was carried out for 40 \*\* and three days after the lamination. This film was made into the pouch in which the inside dimension angle of 15 cm carried out the four-quarters seal. Contents were used as water. The retort device (Hisaka Works Make, high-temperature-high-pressure cooking sterilization testing machine RCS-40RTGN) was used for this, and 95 \*\* and germicidal treatment for 30 minutes were carried out. In particular as for the pouch after germicidal treatment, the defect was not observed in appearance and a gestalt.

[0050]When the gestalt (the diameter of a weighted mean flake, a weighted mean aspect ratio) of the talc which calcinated and obtained the interlayer of the pouch with the electric furnace was observed with the scanning electron microscope, the thing and \*\*\*\*\* difference before mixing were not accepted. The places where a pouch is arbitrary and which cut off several places and observed the interlayer of the section with the scanning electron microscope, Many fields which did not condense talc, and the film of talc has laminated almost in parallel with an intermediate layer film side, and have been laminated were also seen, and the dispersibility (it is presumed that it is acting on the fall of the permeability of oxygen gas) of talc was good further again. The above result is shown in Table 1.

[0051]Except having changed Example 2 - the blend rate of 3EVOH and talc at a rate shown in Table 1, the pouch which makes a film and this film an interlayer like Example 1 was created, and same measurement was carried out. A result is shown in Table 1.

[0052]The saponification degree of 31 mol of example 4 ethylene-content % and a vinyl acetate component 99.5-mol %, Except that MI used 1.6g/EVOH for 10 minutes vinyltrimetoxysilane 0.027 mol%, the pouch which makes a film and this film an interlayer like Example 1 was created, and same measurement was carried out. A result is shown in Table 1.

[0053]Except having changed the diameter of a weighted mean flake of example 5 talc, and the weighted mean aspect ratio, as shown in Table 1, Bouch who makes a film and this film an interlayer like Example 1 was created, and same measurement was carried out. A result is shown in Table 1.

[0054]In comparative example 1 Example 1, do not blend talc but 31 mol of ethylene content %, Except that the saponification degree of the vinyl acetate component used 99.5-mol % and MI used 1.6g/the EVOH independent for 10 minutes, the pouch which makes a film and this film an interlayer like Example 1 was created, and same measurement was carried out. The dimensional change was large at the time of heating, and the appearance after germicidal treatment also got worse. A result is shown in Table 1.

[0055]Except that the saponification degree of 31 mol of comparative example 2 ethylene-content % and a vinyl acetate component used 90.0-mol % and MI used 8.5g/EVOH for 10 minutes, it was going to carry out the same measurement as Example 1, but gel and BUTSU occurred frequently at the time of film production of a constituent, and various evaluations were not completed. A result is shown in Table 1.

[0056]MI which the saponification degree of 17 mol of comparative example 3 ethylene-content % and a vinyl acetate component measured at 210 \*\* 99.5-mol% used 7.5g/EVOH for 10 minutes, created the pouch which makes a film and this film an interlayer like Example 1, and carried out same measurement. Probably because the dispersibility of talc fell and moisture resistance was inferior, the appearance after germicidal treatment also got worse. A result is shown in Table 1.

[0057]Except having changed the blend rate of comparative example 4EVOH and talc at a rate shown in Table 1, the pouch which makes a film and this film an interlayer like Example 1 was created, and same

measurement was carried out. The appearance of a monolayer film, the dispersibility (condensation of talc was seen in part) of talc, and the appearance after germicidal treatment were inferior. A result is shown in Table 1.

[0058] Although it was going to test like Example 1 except having changed the blend rate of talc of comparative example 5EVOH at a rate shown in Table 1, the mobility at the time of melting is bad, kneading is difficult, and blend pelletizing of EVOH and talc was not completed. A result is shown in Table 1.

[0059] Except having used what was enough washed with pure water as comparative example 6EVOH, the pouch which makes a film and this film an interlayer like Example 1 was created, and same measurement was carried out. Moisture vapor transmission was large and the appearance after germicidal treatment was also inferior. A result is shown in Table 1.

[0060]

[Table 1]

	EVOH(E)				タルク(T)[*1]		E/T
	エチレン	けん	MI	Tm	重量平均	重量平均	
	含量	化度			フルーク径	アスペクト比	
	(モル%)	(モル%)	(g/10分)	(℃)	(μ)		(重量比)
実施例 1	31	99.5	1.6	183	3	15	80/20
実施例 2	31	99.5	1.6	183	3	15	70/30
実施例 3	31	99.5	1.6	183	3	15	60/40
実施例 4[*2]	31	99.5	1.6	183	3	15	80/20
実施例 5	31	99.5	1.6	183	10	10	80/20
比較例 1	31	99.5	1.6	183	-	-	100/0
比較例 2	31	90.0	8.5	158	3	15	80/20
比較例 3	17	99.5	7.5[*3]	207	3	15	80/20
比較例 4	31	99.5	1.6	183	3	15	45/55
比較例 5	31	99.5	1.6	183	3	15	25/75
比較例 6	31	99.5	1.6	183	3	15	80/20

\*1 混練前の原料タルクの特性値。

\*2 実施例 4 の EVOH は共重合成分ビニルトリメトキシシラン 0.027モル%

含有している。

\*3 210℃, 2160 g の荷重条件下で測定

[0064]

## \* NOTICES \*

JP0 and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

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**CLAIMS**


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[Claim(s)]

[Claim 1]It consists of a layer of a resin composition which consists of 50 to 95 % of the weight of ethylene-vinyl alcohol system copolymers, and 50 to 5 % of the weight of inorganic fillers, Many fields where a two-dimensional film has laminated an inorganic filler in parallel with the direction of a stratification plane of said layer substantially are included in said copolymer in said layer, And a diameter of a weighted mean flake of an inorganic filler in this field is 30micro or less, a weighted mean aspect ratio is three or more, moisture vapor transmission of said layer satisfies a following (I) type further, and it is a rate of a dimensional change (in the air) further. A film whose value measured after melting point-40 \*\* and 60-minute processing

$$W \leq \sum_{i=0}^5 (A_i \cdot E^i) \quad (I)$$

is -2.5%~+2.5%.

Here, content (mol %) of moisture vapor transmission [ in / in W / temperature of 40 \*\* and 90% of a relative humidity difference ] (g.30micro/[m ]<sup>2</sup> and day) and an ethylene ingredient of said copolymer [ in / in E / said film layer resin ] and A<sub>i</sub> (i= 0-5) are constants given below.

$$A_0 = 1.105 \times 10^3, A_1 = 8.150 \times 10^2, A_2 = 2.420 \times 10^{-2}, A_3 = 3.535 \times 10^{-2}, A_4 = 2.530 \times 10^{-4}, A_5 = 7.091 \times 10^{-7} \text{ [Claim 2] } A$$

multilayer film which makes an interlayer a layer of the resin composition according to claim 1, and has a layer of damp-proof thermoplastics in this interlayer's inside-and-outside layer.

[Claim 3]A packing material for voile sterilization or retort sterilization which consists of the film according to claim 1 or 2.

[Claim 4]A packed body which was voile-sterilized, or carried out retort sterilization, and was obtained after filling up with and sealing contents to a packing material which consists of claim 1 and a film given in 2.

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[Translation done.]

[Table 2]

	中間層(EとTのブレンド層)			中間層の加熱寸法変化率		多層フィルム の外観 (トリート後)
	透湿度W [＊4]	りん酸化合物量 (ppm)	タルクの 分散性	縦方向	横方向	
実施例 1	35(64)	45	○	-1.7	0.5	○
実施例 2	29(64)	40	○	-0.9	0.3	○
実施例 3	26(64)	35	○	-0.6	0.2	○
実施例 4	34(64)	45	○	-1.3	0.1	○
実施例 5	38(64)	45	○	-1.5	0.4	○
比較例 1	69(64)	55	—	-10.4	8.3	×
比較例 2	155(64)	—	—	—	—	—
比較例 3	—	—	△	-3.9	1.9	×
比較例 4	—	—	×	-1.1	1.5	×
比較例 5	—	—	—	—	—	—
比較例 6	66(64)	2	○	-2.9	0.5	△

\*4 単位は $\text{g} \cdot 30 \mu / \text{m}^2 \cdot \text{day}$ 、( )内は本文 I 式に基づいて計算した値。

\*5 ○ 外観変化なく、良好

△ パウチ表面にしわ、たるみ模様が一部発生

× パウチ表面にしわ、たるみ模様がかなり発生

\*6 ○ 凝集物なし

△ 凝集物わずかみられる

× 凝集物かなりみられる

[0062]

[Effect of the Invention] After filling up with and sealing foodstuffs to the packing material which consists of a film of this invention, or a multilayer film, the food packaging body produced by carrying out germicidal treatment under heat, such as voile sterilization and retort sterilization, and the conditions on which moisture acts simultaneously is excellent in the appearance after germicidal treatment.

[Translation done.]